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A SAXS Study of PHB/DGEBA Blends Crystallized at Different Temperatures

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Abstract

A small-angle X-ray scattering (SAXS) study of blends of poly-3-hydroxybutyrate (PHB)/diglycidyl ether of bisphenol A (DGEBA) with weight ratios of 90/10, 70/30 and 50/50 and PHB isothermally crystallized at temperatures between 60ºC and 120ºC for one hour was performed. PHB was studied at different temperatures between 30ºC and 140ºC. The scattering curve results (intensity as a function of scattering vector (q)) indicated a main peak and secondary peaks associated with the thickness of the lamellae of PHB (with a strong tendency to crystallization). The position of the main peak decreased when the temperature was increased. At high temperatures (~120ºC), a deformation was observed in the main peak and a secondary peak was superimposed. This secondary peak was associated with the lamellar structures formed during the re-crystallization process. The results are discussed based on the DGEBA inclusion in the blends, crystallization temperature and partial interlamellar segregation.

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1. Introduction

Poly-3-hydroxybutyrate (PHB) is a polyester of bacterial origin with increasing importance due to its biodegradable properties and it being a product of biomass. In the last few years and with the aim of replacing typical synthetic polymers, there has been increasing interest in the study of different aspects of PHB. The crystallization process and the structures formed in PHB are issues that are of great interest to researchers due to its potential applications. The crystallization of PHB through intermediate states including density fluctuations, mesomorphic states and crystals has been reported in the literature by Guo et al. (2012). In addition, a melting, re-crystallization and re-melting process has been observed in PHB. The study of such a process via calorimetric technique, as an example, is complex. Calorimetric results have shown different peaks associated with melting that eventually become superimposed, which corresponds to melting of the original crystals and melting of the crystals formed upon re-crystallization (Pearce and Marchessault (1994)). The discontinuity in the PHB lamellar parameters of single crystals as a function of temperature was reported by Sawayanagi et al. (2006). This process was associated with melting and re-crystallization and allowed for the formation of new crystals with dimensions that were greater than the original crystals. However, it was noted that these crystals were prepared in solution unlike the present study where the aim is to analyze if a discontinuity in the lamellar parameters is also observed in crystals formed from melts of the blends.

In addition, the diglycidyl ether of bisphenol A (DGEBA) is one of the monomers used to develop epoxy networks. Therefore, the study of PHB/DGEBA blends is performed to develop PHB/epoxy blends. Because the highest PHB crystallization speed under isothermal conditions is produced at approximately 80ºC (Barham et al. (1984)) and for the cure of DGEBA-anhydride epoxy resins temperatures between 80ºC and 140ºC are usually used, became possible the growth of crystals during the cure process of PHB/epoxy blends. This result is relevant to the final microstructure of the polymer, and therefore, an important goal of future research is to gain insight into the development of lamellae during the isothermal process at a temperature of approximately 80ºC in PHB blending with DGEBA.

In the present work, the lamellar structure in PHB/DGEBA blends and plain PHB crystallized at 60ºC, 80ºC and 100ºC is studied using a small-angle X-ray scattering (SAXS) experimental technique. In addition, in plain PHB, SAXS measurements are performed at various temperatures between 30ºC and 140ºC.

2. Experimental

The samples were prepared with PHB BIOCYCLE supplied by PHB INDUSTRIAL SA (Brazil) and DGEBA Araldite My790 supplied by Hunstman. The PHB/DGEBA blends were melted in a glass test tube by increasing the temperature to 180ºC and stirring during the entire process. Next, the blends inside the tube were cooled quickly to the crystallization temperature and thermo-stabilized at crystallization temperature, T_c, in an oil bath for 1 hour. Samples with PHB/DGEBA weight ratios of 100/0, 90/10, 70/30 and 50/50 were prepared. The results obtained from differential scanning calorimetry have shown that under isothermal conditions similar to those used in this work, the crystallization occurs in less time than the that required in the current work (Silva (2013)).

The SAXS measurements were performed at the Brazilian Synchrotron Light Laboratory (LNLS) CNPEM/MCT, line SAXS1 Campinas, Brazil. A wavelength of $\lambda = 1.55$ Å was selected for the monochromatic beam used in the experiments. The scattering angle (2θ) was selected for the scattering vector (q):

$$q = \frac{4\pi}{\lambda} sen(\theta) \tag{1}$$

between 0.16 $nm^{-1} \leq q \leq 3$ nm^{-1}. The measurements at the desired temperature were performed using a hot-stage cell THM 600, Linkam Ltd. assembled on the SAXS1 line (for experimental details see Plivelic et al. (2005)). The scattering curves were recorded with a 2-D detector with a spatial resolution of 172 μm located at a distance of 627 mm from the samples. The 2-D scattering profiles were averaged at several radii and converted to 1-D data using the FIT2D V12.077. For the measurements, the samples were sealed in modified DSC pans with Kapton windows. The

SAXS measurements were performed at different temperatures in successive steps of 10°C at a rate of 20ºC/min. The measurement time was 15 s. Prior to taking measurements, the samples were maintained for 2 min at a constant temperature for thermo-stabilization after each temperature step. A set of measurements was performed to observe possible changes in the sample due to radiation exposure. However, variations were not observed in the spectra obtained.

3. Results and Discussion

3.1. Blends crystallized at different temperatures.

SAXS measurements were performed on the PHB and PHB/DGEBA blends with different proportions and crystallized at temperatures of 60°C, 80°C and 100°C. In Figs. 1a, 1b, 1c and 1d, the results of pure PHB, PHB/DGEBA 90/10, PHB/DGEBA 70/30 and PHB/DGEBA 50/50, respectively, are shown in plots $I.q^2$ as a function of q.

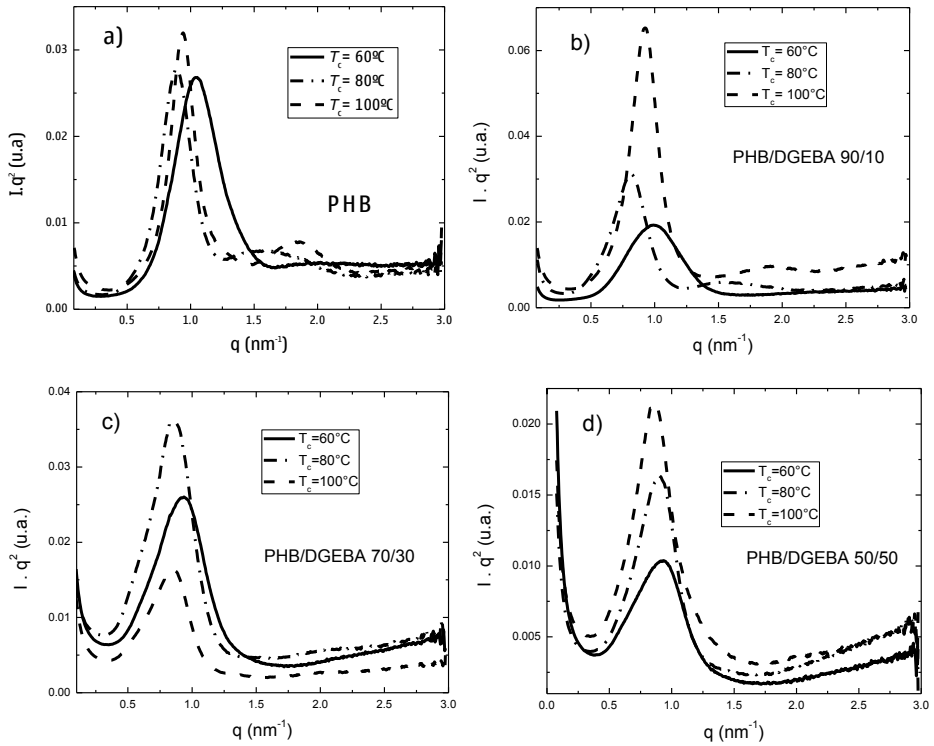

Fig 1. SAXS curves for $I\,q^2$ as a function of q obtained for samples crystallized at different temperatures. a) PHB, b) PHB/DGEBA 90/10 blend, c) PHB/DGEBA 70/30 blend and e) PHB/DGEBA 50/50 blend.

In Fig. 1a, a main peak and secondary peaks are observed for pure PHB. The main peak is observed at q values of 1.04 nm^{-1}, 0.89 nm^{-1} and 0.94 nm^{-1} for samples crystallized at 60ºC, 80ºC and 100ºC, respectively. The secondary peaks are observed at q values of 2.01 nm^{-1}, 1.56 nm^{-1} and 1.86 nm^{-1}. The secondary peak associated with the sample crystallized at 60°C has a lower intensity than that corresponding to the secondary peak in the other samples.

The presence of secondary peaks in the SAXS spectra has been discussed in the literature, and some authors have attributed these peaks to high-order scattering (Heo et al. (2008)). However, the results shown in Fig. 1 indicate that

the intensity of the secondary peak depends on the crystallization temperature. Therefore, this peak may be associated with the properties of the material. Hama and Tashiro modeled the crystallization of polyoxymethylene as a primary and a secondary crystallization where there is an insertion of lamellae within the original lamellae (Hama and Tashiro (2003 and 2003b)). Therefore, the secondary peaks may be associated with the lamellae that developed during the secondary crystallization with thickness lower than the thickness of lamellae developed during primary crystallization.

In Figs. 1b, 1c and 1d, the SAXS curves for PHB/DGEBA 90/10, PHB/DGEBA 70/30 and PHB/DGEBA 50/50 are shown. These curves also exhibit a main peak and a secondary peak, but the secondary peak has a lower intensity in the blends with the highest DGEBA content. A lower intensity of the secondary peak was observed for the blends crystallized at 60°C compared to the results obtained for blends crystallized at other crystallization temperatures, and effectively, the secondary peak is not observed for the PHB/DGEBA 50/50 blend. These results indicate that the generation of secondary lamellae decreases as the DGEBA content in the blend increases.

The average long period of a lamella can be estimated from the maximum of the peak in the SAXS curve by:

$$L = \frac{2\pi}{q_{\max}} \tag{2}$$

In Fig. 2, the L values obtained from eq. 2 as a function of the PHB content are shown for the different crystallization temperatures. For crystallization at 60°C, L is approximately constant when the PHB content increases from 50% to 70% but decreases when the PHB content increases from 70% to 100%. For the samples crystallized at 80°C and 100°C, L exhibits a behavior with a maximum in PHB content of 90% for crystallization at 80°C and 70% for crystallization at 100°C. Based on these results, it could be assumed that for the sample crystallized at 60°C, there is a maximum in the plot L as a function of PHB content between 50% and 70%. Therefore, for all of the samples, there is an increase in L when DGEBA is added to PHB, and it reaches a maximum for a PHB content that depends on crystallization temperature.

Recently, the authors reported the lamellar thickness for PHB/DGEBA blends crystallized at room temperature, and they found that L exhibits a behavior as a function of the PHB content with a maximum in 70% (Silva et al. (2013)). L was determined to increases when DGEBA is added (up to 30%) to the blend due to an increase in the amorphous thickness. This increment was attributed to the inclusion of DGEBA within the lamellar amorphous component. However, for DGEBA content higher than 30%, the DGEBA would segregate toward regions outside the lamellae. This explanation could be extended to samples crystallized at temperatures between 60°C and 100°C studied in this work.

The value of L at the maximum is approximately 10% higher than the value of L for pure PHB at the same crystallization temperature. The lamellar structure does not support an increase in the thickness higher than 10% when DGEBA is added to the blend. Otherwise, the DGEBA segregates out of the lamella.

The PHB/DGEBA blend is miscible in the melt state for the whole range of compositions (Silva et al. (2013)). For blends with a high PHB content, segregation of DGEBA toward amorphous regions next to the crystalline regions occurs when crystallization begins. Therefore, the thickness of the amorphous component increases resulting in an increase in L. For blends with a low PHB content, the DGEBA segregates toward amorphous regions out of the lamellae (interfibrillar regions), and L is not affected. Notably, in the last process, there is a decrease in L when the PHB content decreases. Therefore, DGEBA could be readily drawn towards regions outside of the lamellae. The limit between low or high PHB content given for the position of the maximum L as a function of the PHB content depends on the crystallization temperature.

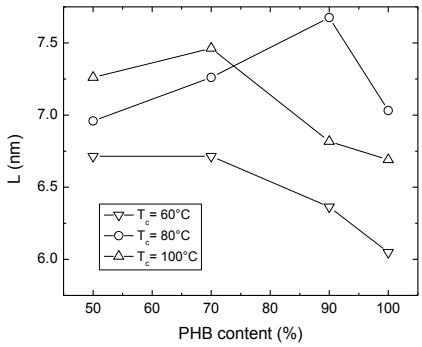

Fig. 2. *L* as a function of PHB content for different crystallization temperatures.

3.2. PHB measurements at several temperatures.

The SAXS measurements were performed at different temperatures between 30°C and 140ºC for the pure PHB samples isothermally crystallized at 60°C, 80°C and 100°C. In Figs. 3a, 3b and 3c, the results obtained are presented as plots of $I.q^2$ as a function of q. The main peak shifts to lower q values when the temperature increases. However, at temperatures higher than 120°C, the main peak is deformed, and a superposition of peaks most likely occurs.

The secondary peaks located between 1.0 $nm^{-1} < q < 2.5$ nm^{-1} shift toward lower q values when the temperature increases. To provide better visualization, this region is presented independently in Figs. 3d, 3e and 3f, which correspond to T_c=60ºC, T_c=80ºC and T_c=100ºC, respectively. At temperatures higher than 120°C, evidence of an incipient and barely defined new peak located at 1.35 nm^{-1}, 1.40 nm^{-1} and 1.28 nm^{-1} for samples crystallized at 60ºC, 80ºC and 100ºC, respectively, are observed.

The superposition of peaks at high temperatures can be associated with the presence of new peaks located at q values lower than that corresponding to the peaks observed at low temperatures. This peak may correspond to scattering in the lamellae formed during heating, which are thicker than the original lamellae. Sawayanagi et al. (2006) reported a discontinuous thickening of L when the temperature was increased to approximately 120°C in single crystals growth from solution. The discontinuous thickening of L was associated with the growth of lamellae caused by partial melting and re-crystallization.

The new peaks observed in the region 1.0 $nm^{-1} < q < 2.5$ nm^{-1} at temperatures higher than 120°C may indicate that secondary crystals form within interlamellar regions during the re-crystallization.

Notably, in this work and in contrast to the work of Sawayanagi et al. (2006), the crystals were grown in polycrystalline samples from melt. Although the results from both studies are similar, there are some differences. In the current study, the peaks are broader than those in the results reported in literature, which is most likely due to the existence of multiple crystals that produce more diffuse scattering.

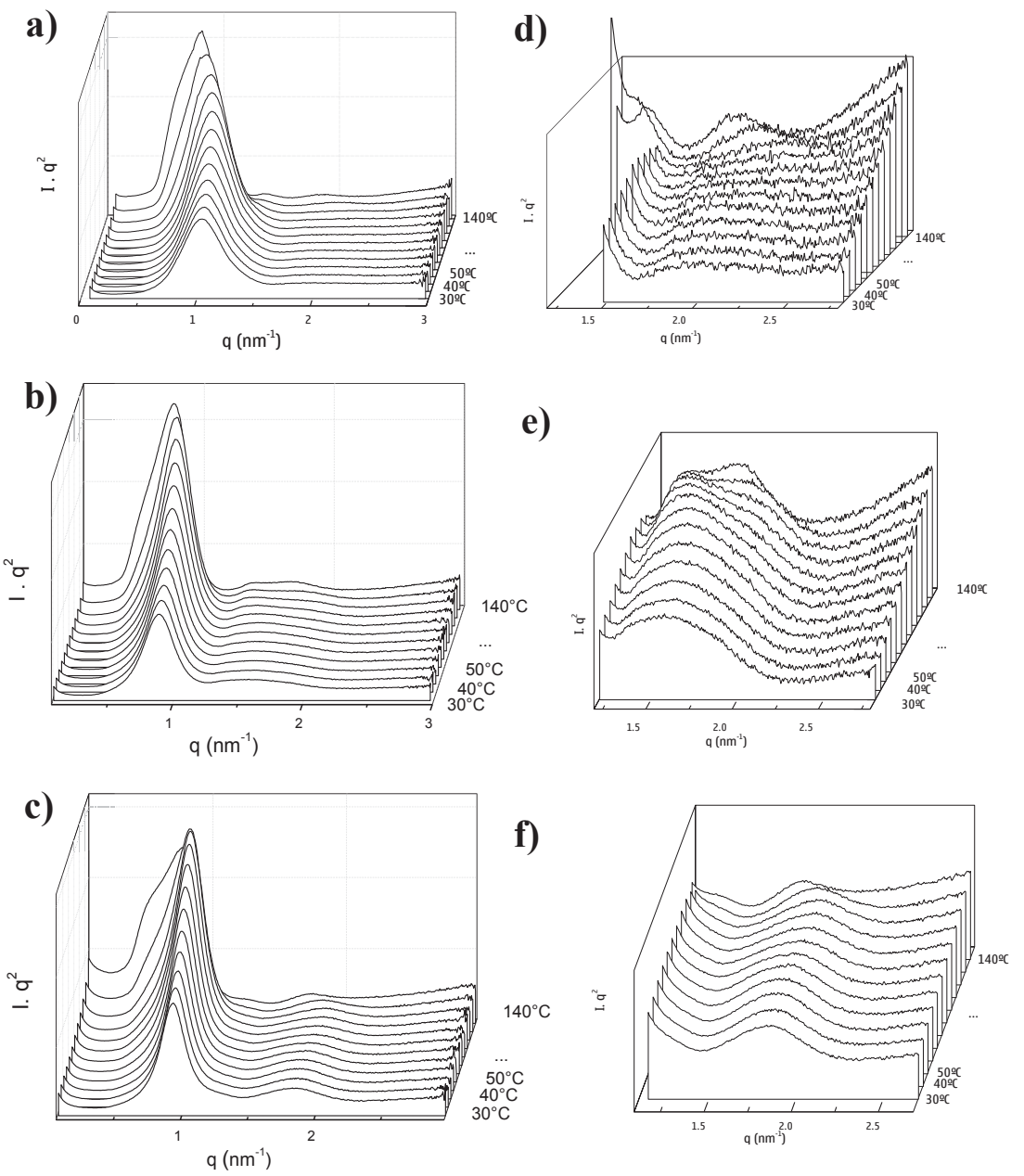

Fig. 3. SAXS curves for $I.q^2$ as a function of q obtained at different temperatures for the PHB samples crystallized at: a) 60ºC, b) 80ºC and c) 100ºC. Magnification of the range 1.4 $nm^{-1} < q < 3.0$ nm^{-1} for PHB samples crystallized at: d) 60ºC, e) 80ºC and f) 100ºC.

4. Conclusions

The SAXS results obtained for the PHB and PHB/DGEBA samples crystallized at several temperatures are reported. A main peak associated with the lamellar structure and secondary peaks located in the q range of 1.0 nm^{-1} to 2.5 nm^{-1} associated with secondary lamellae were observed. The lamellar period (L) was calculated, and a

maximum as a function of PHB content was observed. The position of the maximum depends on the crystallization temperature. This behavior was attributed to an increase in the lamellar thickness due to the inclusion of DGEBA within the amorphous interlamellar regions for low DGEBA content but it is segregated out of lamellae at higher DGEBA contents.

The SAXS results obtained at several temperatures between 30°C and 140°C for the PHB samples crystallized at different temperatures are reported. At temperatures higher than 120°C, there is superposition of the peaks, which is due to the formation of lamellae during melting and re-crystallization. New peaks, which are located in the q range of 1.0 nm^{-1} to 2.5 nm^{-1}, were formed at temperatures higher than 120°C. These peaks could be attributed to formation of secondary lamellae during re-crystallization with thickness lower than the main lamellae.

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